INFRARED SPECTRA OF SODIUM FORMATE-d

by

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INTRODUCTION

The absorption or emission spectrum arising from the rotational and vibrational motions of a molecule which is not electronically excited is mostly in the infrared region (24). According to classical electrodynamics (9), any motion of an atomic system that is connected with a change of its dipole moment leads to the emission or absorption of radiation.

During the vibrational motion of a molecule the charge distribution undergoes a periodic change, and, therefore, in general the dipole moment changes periodically. Since in the harmonic oscillator approximation, any vibrational motion of the molecule may be resolved into the sum of normal vibrations, and since the normal vibrations are the only simple periodic motions, the normal vibrational frequencies are equal to the radiant frequencies that are emitted or absorbed by the molecule. These frequencies often lie in the near-infrared, i.e., 4000-600 $cm.^{-1}$. It is usually the absorption spectrum that is observed in the infrared.

Normal vibrations that are connected with a change of dipole moment and, therefore, appear in the infrared are called "infrared active." Those vibrations for which the change of charge distribution is such that no change of dipole moment arises, and which, therefore, do not appear in the infrared, are called "infrared inactive." In the harmonic oscillator approximation only the fundamental frequencies, ν_i, are active. Although overtones ($n_i \nu_i$) and combinations ($n_i \nu_i + n_k \nu_k$), (where n_i and n_k are vibrational quantum numbers for the ith and kth fundamentals, respectively) are inactive in the harmonic approximation, both types of vibrations are observed due to anharmonicity in the vibrational potential energy.

A polyatomic molecule consisting of N nuclei has 3N-6 (if non-linear) or 3N-5 (if linear) normal modes of vibration and these are unambiguously determined by solving the vibrational secular equation if the force constants are known. However, the actual calculation of the normal modes may be difficult if the secular equation is of a high order. Only in very few cases (14) is it feasible to obtain the values of the potential constants of a polyatomic molecule on a purely theoretical basis, and to then predict the vibrational frequencies by solving the secular equation (1). In most cases one must determine the potential constants (or force constants) from the experimentally observed fundamental frequencies of the particular molecule. However, in all except a very few cases the number of potential constants is larger than the number of normal vibrations (3N-6) and therefore the former cannot all be determined from the latter (10). One way to circumvent this difficulty is by the investigation of isotopic molecules for which the potential constants are the same (at least to a very high approximation) but the frequencies are different. Thus, additional data are obtained for determination of the potential constants. Another approach is to make specific assumptions about the forces in the molecules such that the number of force constants to be determined is reduced. Either approach requires a correct assignment of observed frequencies to 3N-6 possible fundamentals.

A commonly used simplification of the molecular force field is the assumption of valence forces which was first made by Bjerrum (3). He assumed that there is a strong restoring force in the line of every valence bond if the distance of the two atoms bound by this bond is changed. In addition he assumed that there is a restoring force opposing a change of the angle between two valence bonds connecting one atom with two others.

The infrared spectra of polycrystalline alkali metal and alkaline earth formates have been measured (8) in the region of 500 cm^{-1} to 3000 cm^{-1}. Several Raman studies of aqueous solutions of the formate ion (16, 17, 5) have been reported. Thomas (22) has reported studies of the carbonyl group in the formate ion. Newman (18) has obtained polarised infrared spectra of single crystals of sodium formate. Ito and Bernstein (15) have obtained infrared spectra of the formate ion for both the solid and aqueous solutions. They have also obtained Raman spectra of these ions with depolarization ratios. Hammaker and Walters (6) have reported infrared spectra of C-13 enriched sodium formate in solution, mull and pellet, and have proposed vibrational assignments based on the product rule and relative intensities for all fundamentals and some binary combinations of the formate ion.

The assignments of Hammaker and Walters (6) would be more convincing if complete infrared data for the formate-d ion were available for product rule calculations. Although the Raman spectra of aqueous solutions of sodium formate-d have been obtained by Fonteyne (5), the infrared spectra of the formate-d ion in aqueous solution are not available. Pellet spectra of sodium formate-d measured by Harvey, et al. (8) give an inconclusive result in the product rule calculation, although they tend to favor an earlier assignment of Newman (18) for ν_2 and ν_5 rather than the more recent assignment by Ito and Bernstein (15) and Hammaker and Walters (6). Raman data of Fonteyne for the formate-d ion combined with infrared data of Hammaker and Walters for the formate ion in solution give a product rule result which favors the assignment by Ito and Bernstein and by Hammaker and Walters.

The purpose of this investigation is to obtain solution infrared spectra of the formate-d ion for comparison with Raman data of Fonteyne and to obtain mull and pellet spectra of this ion for comparison with the pellet data of

Harvey et al. These data for the formate-d ion will complete the infrared investigation of the three isotopic ions, formate, formate-^{13}C, and formate-d in this laboratory and will permit three separate product rule calculations (formate with formate-d, formate with formate-^{13}C, and formate-^{13}C with formate-d) as a check on the assignment of fundamentals. In addition, the determination of valence force field (VFF) force constants for the three isotopic ions will be made to test the suitability of the valence force field for the formate ion.

EXPERIMENTAL

Materials

Sodium formate-d. Sodium formate-d, 98% deuterated, was obtained from Stohler Isotope Chemicals, 4180 Courtrai Street, Montreal, Canada.

Potassium Bromide. The Harshaw Chemical Co. infrared quality, powdered, potassium bromide was used as received and stored in a desiccator over "Drierite" when not in use.

Deuterium Oxide (Heavy Water). Bio-Rad Laboratories Heavy Water containing 99.77 mole % D_2O was used as received.

Hexachloro-1, 3 - butadiene. Eastman Organic Chemicals technical grade hexachloro -1,3 - butadiene was used as a mulling agent.

Nujol. Nujol, obtained from Plough Inc., was used as a mulling agent.

Sample Preparation

Solutions were made in volumetric flasks by dilution of a known quantity of sodium formate-d with ordinary distilled water, or heavy water, as needed.

To prepare pellets, appropriate amounts of the formate and potassium bromide were ground with a mortar and pestle to form a homogeneous mixture. This mixture was then put in the cavity cut from the center of several pieces of blotter page with a cork borer. The pieces of blotter paper were placed between sheets of aluminum foil and subjected to a pressure of about 16,000 p.s.i.g. (for about four minutes) by means of Carver Laboratory Press, Model B. The resulting pellet was IR-transparent.

Mulls were produced by grinding the powdered formate with small amounts of the mulling agent between rock-salt plates. The quality of the mulls was verified by spectra taken with a Perkin-Elmer Model 237 Spectrometer.

Spectra

The spectra of sodium formate-d were taken with a Perkin-Elmer Model 221 PG Spectrometer. This instrument is an automatic recording, double-beam infrared spectrometer utilizing a servo-driven attenuator to produce a true radiation null in the detector. It includes programmed slit-operation, programmed scan speed, automatic speed suppression, automatic gain control, and ordinate scale expansion and compression. Abscissa presentation is linear in wave numbers, and ordinate presentation is linear in transmittance over a 20 cm. scale.

Table 1 lists the instrument settings when spectra were taken.

Spectra were obtained for aqueous solution (H_2O and D_2O), mulls (nujol and hexachloro-butadiene) and KBr pellets. Frequency measurements were made on an expanded scale (gear combination) of 1 $cm.^{-1}$ per mm. Ammonia, indene, polystyrene, carbon monoxide, carbon dioxide, and hydrogen chloride were used for frequency calibration.

Table (1). Perkin-Elmer 221 PG Infrared Spectrometer settings.

Suppression	3.2
Expansion	1X
Attenuator speed	110
Resolution Amplifier gain	5.3
Slit	Program
Filter	Auto
Slit Program	9.27
Source Intensity	0.32 amp.
Energy	A Gc off
Scan Time	16
Abscissa Expansion	a) For survey spectra 10 $cm.^{-1}$ per mm scale division. b) For accurate measurements 1 $cm.^{-1}$ per mm scale division.

Table (2) gives the frequency ranges where the various calibration materials were used.

Table (2). Frequency Ranges and the Calibration Materials Used.

Frequency Range	Material Used	Sampling Conditions
2800 - 2600	Hydrogen chloride	7.5 cm. gas cell at 400 mm Hg
2450 - 2250	Carbon dioxide	7.5 cm. gas cell at 43 mm Hg
2250 - 1900	Polystyrene	Film
2200 - 2000	Carbon monoxide	7.5 cm. gas cell at 414 mm Hg
1700 - 1500	Polystyrene	Film
1426 - 1300	Indene	0.0015 cm. liquid cell
1150 - 800	Ammonia	7.5 cm. gas cell at 190 mm Hg
850 - 700	Ammonia	7.5 cm. gas cell at 190 mm Hg

The solution spectra were obtained with Irtran-2 window cells with a path length of 0.0015 cm.

RESULTS AND DISCUSSION

Background

The formate ion has been shown by X-Ray analysis (26) to have the general structure XYZ_2. A molecule, just as any geometrical figure, possesses a definite symmetry. The relative positions and the type of the nuclei determine this symmetry. The molecule may have one or more symmetry elements, such as planes of symmetry, a centre of symmetry, and axes of symmetry. To each symmetry element there corresponds a symmetry operation, a coordinate transformation (reflection and/or rotation) that will produce a configuration of the nuclei indistinguishable from the original one. The formate ion, whose coordinate system is shown in Fig. (1), has the symmetry elements shown in Fig. (2). Here σ_v and σ_v' are planes of symmetry, and C_2 is a two-fold rotation-axis of symmetry. The formate ion possessing these elements of symmetry, in addition to the identity element, is said to belong to the C_{2v} point group. A point group is a collection of symmetry operations which fulfill the postulates for the existence of a mathematical group. The identity operation (do nothing) is a member of all groups.

By methods of group theory (4), character tables have been obtained for all symmetry point groups (23). In a character table, the columns refer to the class of symmetry operations, and the rows refer to irreducible representations.

The entries in the table are the characters for the irreducible representations. The character is the sum of the diagonal elements in the matrix which represents an operation. The members of a class of symmetry operations all have the same character. For the C_{2v} point group each operation is in a class by itself. The irreducible representations of a group are the collections

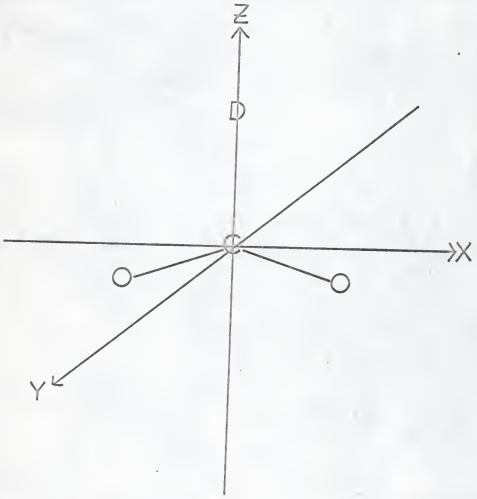


Figure 1. Coordinate system for formate-d ion; Y axis is perpendicular to the plane of paper.

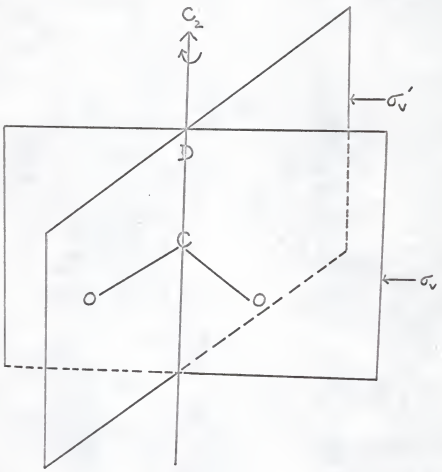


Figure 2. Symmetry elements for formate-d ion.

of simplest possible (i.e., smallest dimensioned) matrices that illustrate the effect of the collection of symmetry operations that form the group. For the C_{2v} point group the irreducible representations are all non-degenerate so that each matrix has a single element which equals its characters.

The fundamental theorem concerning irreducible representations states that for each point group only a definite small number of non-equivalent irreducible representations are possible. The character table for C_{2v} point group is given in Table (3).

Table (3). Character Table for Irreducible Representations of C_{2v} Point Group.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_z	yz

The character tables also assign the translational and rotational coordinates of the center of gravity of the molecule to the proper irreducible representations. These translational and rotational coordinates are represented by x, y, z, and Rx, Ry, Rz, respectively, in Table (3). The last column of Table (3) assigns the polarizability components to the proper irreducible representations. The values of the characters (+1,-1) determine whether coordinates belonging to a given irreducible representation transform into themselves or into the negatives of themselves upon application of a symmetry operation. For example, x and R_y are left unchanged by the E and $\sigma_v(xz)$ operations, and change sign for the C_2 and $\sigma_v(yz)$ operations.

Given the characters of the reducible representations formed by the coordinates of one set of atoms one can proceed to calculate the number of modes of motion (vibrational, rotational, and translational) belonging to each irreducible representation contributed by that set of atoms (19). The fundamental equations involved are:

$$N_k^j = \frac{1}{h} \sum_R \chi^j(R) \chi_k(R) \qquad (1)$$

where N_k^j = number of modes of the kth irreducible representation due to jth set of atoms; h = order of the group which equals the number of symmetry operations in the group; j refers to an equivalent set of atoms, which is a set of atoms that are permutted among themselves by the operations of the group; k refers to an irreducible representation; R refers to all symmetry operations of the group and the summation is over all operations of the group; $\chi_k(R)$ refers to the character of the kth irreducible representation for the operation R; $\chi^j(R)$ refers to the character of the reducible representation based on the coordinates of the jth set of atoms for the operation R.

The value of $\chi_k(R)$ is obtained from the Character Table. The $\chi^j(R)$ must be calculated for each molecule. The total number of vibrational modes of kth irreducible representation due to all atoms may be obtained by summing N_k^j over the various sets of atoms and subtracting the number of translations and rotations of that irreducible representation. Thus,

$$N_k = \sum_j N_k^j - t_k - r_k \qquad (2)$$

where j and k have the significance given above; t_k refers to number of translations in kth irreducible representation (obtained from the Character Table); r_k refers to the number of rotations in kth irreducible representation

(also obtained from Character Table).

The total number of modes of kth irreducible representation due to all atoms is given by

$$\sum_j N_k^j = \frac{1}{h} \sum_R \chi(R)\chi_k(R) \tag{3}$$

$$\chi(R) = \sum_j \chi^j(R) \tag{4}$$

where $\chi(R)$ is the reducible representation character based on 3N cartesian coordinates (three for each of N atoms). Also,

$$N_k = \frac{1}{h} \sum_R \chi(R)\chi_k(R) - t_k - r_k \tag{5}$$

We will apply the above mentioned equations to the formate-d ion. The formate-d ion has three sets of equivalent atoms (i.e., sets of atoms which are transformed into each other by the symmetry operations):

set 1: 2 oxygen atoms

set 2: 1 carbon atom

set 3: 1 deuterium atom

The calculation of the $\chi^j(R)$ may be accomplished using the following relations.

$\chi^j(R) = u^j(R)\,(1+2\,\cos\theta)$ for proper rotations

$\chi^j(R) = u^j(R)\,(-1+2\,\cos\theta)$ for improper rotations

where θ is the angle of rotation in the operation. The operations C_n (rotation) are proper rotations with $\theta = 2\pi/n$, while the operations S_n

(rotation reflection) are improper rotations with corresponding θ values. The identity operation E is a proper rotation with θ = 0. $u^j(R)$ is the number of atoms of the jth set left unchanged by symmetry operation R. Table (4) shows the $u^j(R)$ values for the formate-d ion.

Table (4). Formate-d ion. No. of atoms of jth set left unchanged by symmetry operation R.

R =	E	C_2	$\sigma_v(xz)$	$\sigma_{v'}(yz)$
$u^j(R)$ for two oxygens	2	0	2	0
$u^j(R)$ for both one carbon and one deuterium	1	1	1	1

The $\chi^j(R)$ and $\chi(R)$ are calculated as follows:

Set 1: Two oxygens

$\chi^1(E) = 2(1+2) = 6;$

$\chi^1(C_2) = 0(1-2) = 0;$

$\chi^1(\sigma_v) = 2(-1+2) = 2;$

$\chi^1(\sigma_v') = 0(-1+2) = 0;$

Sets 2 and 3: One carbon; one deuterium

$\chi^2(E) = \chi^3(E) = 1(1+2) = 3$

$\chi^2(C_2) = \chi^3(C_2) = 1(1-2) = -1$

$\chi^2(\sigma_v) = \chi^3(\sigma_v) = 1(-1+2) = 1$

$\chi^2(\sigma_v') = \chi^3(\sigma_v') = 1(-1+2) = 1$

$\chi(E) = 6+3+3 = 12$

$\chi(C_2) = 0-1-1 = -2$

$\chi(\sigma_v) = 2+1+1 = 4$

$\chi(\sigma_v') = 0+1+1 = 2$

Hence we can write the character table for the reducible representation based on 3N cartesian coordinates as follows (Table 5):

Table (5). Reducible Representations, Γ's, of Formate-d Ion.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma(O)$	6	0	2	0
$\Gamma(D)$	3	-1	1	1
$\Gamma(C)$	3	-1	1	1
Γ(3N cart.)	12	-2	4	2

From the character table for the irreducible representations, we have for t_k, r_k and h the following:

	A_1	A_2	B_1	B_2	
t_k	1	0	1	1	; h = 4
r_k	0	1	1	1	

The N_k are now calculated from equation (2) as follows:

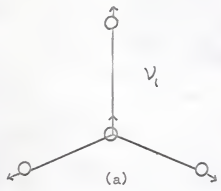
$$N_{A_1} = \tfrac{1}{4}\left[12(1) + (-2)(1) + (4)(1) + (2)(1)\right] - 1 - 0 = 3$$

$$N_{A_2} = \tfrac{1}{4}\left[(12)(1) + (-2)(1) + (4)(-1) + (2)(-1)\right] - 0 - 1 = 0$$

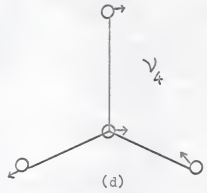
$$N_{B_1} = \tfrac{1}{4}\left[(12)(1) + (-2)(-1) + (4)(1) + (2)(-1)\right] - 1 - 1 = 2$$

$$N_{B_2} = \tfrac{1}{4}\left[(12)(1) + (-2)(-1) + (4)(-1) + (2)(1)\right] - 1 - 1 = 1$$

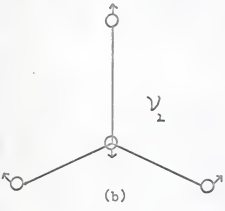
Thus, fundamental modes of vibration are equal to $3A_1 + 2B_1 + B_2$. Fig. (3) gives the normal vibrations of an XYZ_2 molecule (11). Motions perpendicular to the plane of the paper are indicated by + or - signs in the circles representing the particular nuclei. The formate-d ion fundamentals may not



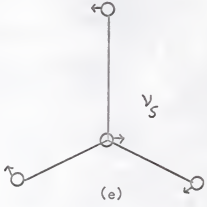
symmetrical C-H stretching



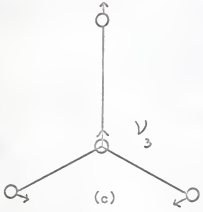
asymmetrical C-O stretching



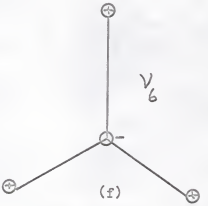
symmetrical C-O stretching



C-H in-plane deformation



symmetrical C-O deformation



C-H bending out of plane

Figure 3. Normal modes of vibrations of formate-d ion.

have the exact form shown in Fig. (3), but they do have the same symmetry.

Observed Frequencies and Assignments

Figures (4 - 12) show the spectra of the fundamental vibrations of sodium formate-d. Table (6) gives the observed frequencies and assignments for fundamentals of sodium formate-d. Table (7) compares our frequencies and assignments for fundamentals of sodium formate-d for IR solution to Raman solution (Fonteyne (5)) and pellet IR to pellet IR (Harvey, et al. (8)). In Table (8) are presented our observed binary combination frequencies and assignments for sodium formate-d. Table (9) compares our frequencies and assignments for combinations with those reported by Fonteyne (5) and Harvey, et al. (8).

Table (6). Observed frequencies and assignments for fundamentals of sodium formate-d.

Assignment	Solution[1]	Mull[2]	Pellet[3]
ν_1 (A_1)	2116	2130	2133
ν_2 (A_1)	1326	1331	1334
ν_3 (A_1)	762	765	768
ν_4 (B_1)	1584	1579	1582
ν_5 (B_1)	1024	1012	1013
ν_6 (B_2)	914	913	915

[1] All frequencies are reproducible to $\pm$ 1 cm.$^{-1}$

[2] ν_3, ν_5, ν_6 are reproducible to $\pm$ 1 cm.$^{-1}$; ν_1, ν_2, ν_4 to $\pm$ 2 cm.$^{-1}$

[3] ν_4 is reproducible to $\pm$ 4 cm.$^{-1}$; others are to $\pm$ 1 cm.$^{-1}$

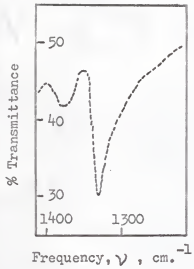


Figure 4. I.R. spectrum of sodium formate-d mull (nujol) in the range 1400-1200.cm.$^{-1}$

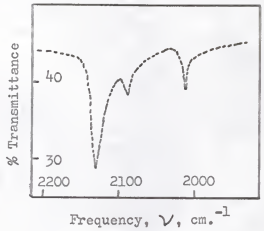


Figure 5. I.R. spectrum of sodium formate-d mull (nujol) in the range 2200-1900 cm.$^{-1}$

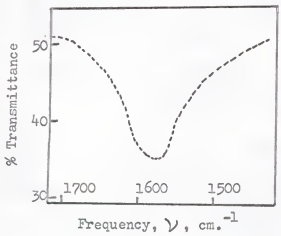


Figure 6. I.R. spectrum of sodium formate-d mull (hexachloro-butadiene) in the range 1700-1500 cm.$^{-1}$

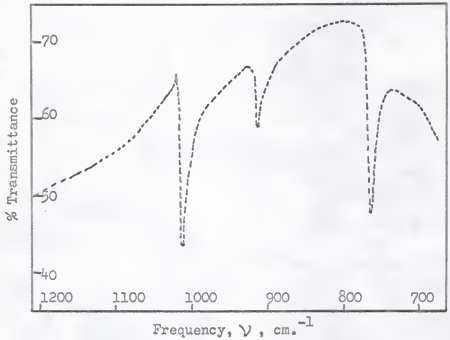


Figure 7. I.R. spectrum of sodium formate-d mull (nujol) in the range 1200-700 cm.$^{-1}$.

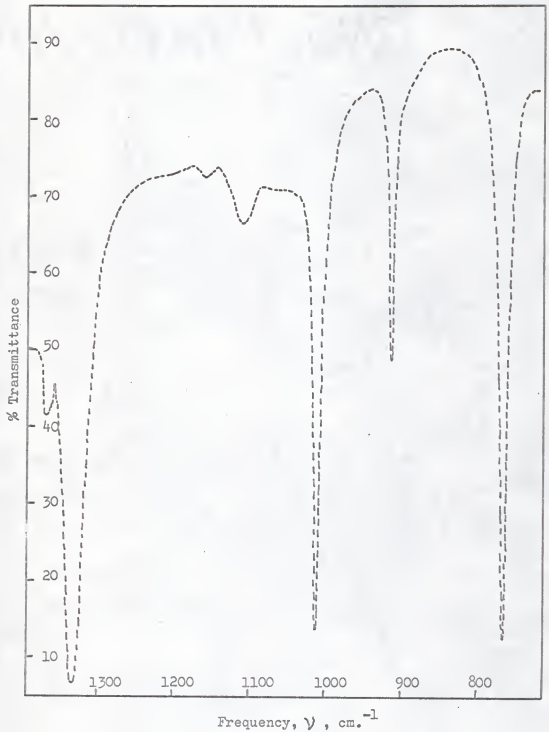


Figure 8. I.R. spectrum of sodium formate-d, 0.56 wgt. % in potassium bromide pellet, in the frequency range 1350-700 cm.$^{-1}$.

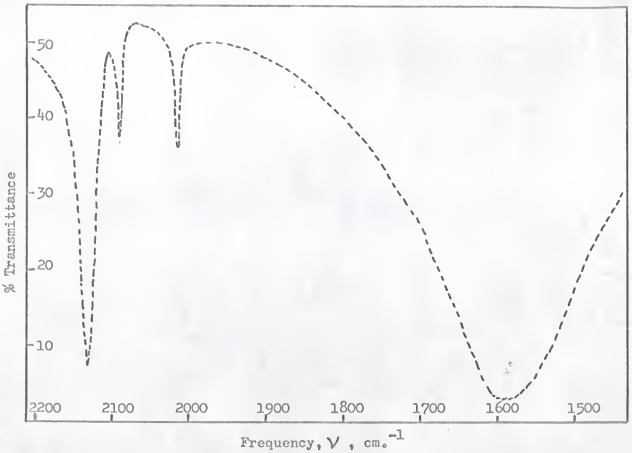


Figure 9. I.R. spectrum of sodium formate-d, 0.56 wgt. % in potassium bromide pellet, in the frequency range 2200-1500 cm.$^{-1}$.

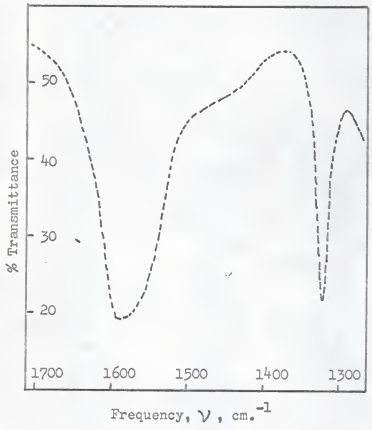


Figure 10. . I.R. spectrum of sodium formate-d, saturated solution in heavy water, in the frequency range 1700-1300 $cm.^{-1}$.

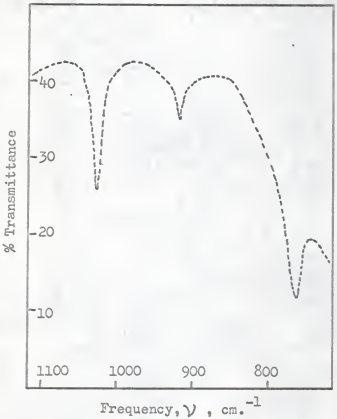


Figure 11. I.R. spectrum of sodium formate-d, saturated solution in heavy water, in the frequency range 1100-700 cm.$^{-1}$.

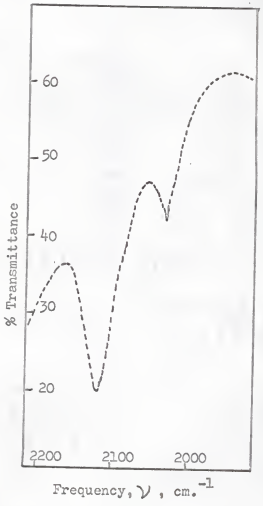


Figure 12. I.R. spectrum of sodium formate-d, saturated solution in heavy water, in the frequency range 2200-1900 cm.$^{-1}$.

Table (7). Comparison of frequencies and assignments for fundamentals of sodium formate-d.

	Solution			Pellet	
	This work (infrared)	Fonteyne (Raman)		This work (infrared)	Harvey et al. (infrared)
$\nu_1(A_1)$	2116	2122	$\nu_1(A_1)$	2133	2130
$\nu_2(A_1)$	1326	1329	$\nu_2(A_1)$	1334	1327
$\nu_3(A_1)$	762	757	$\nu_3(A_1)$	768	762
$\nu_4(B_1)$	1584	1580	$\nu_4(B_1)$	1582	1580
$\nu_5(B_1)$	1024	1028	$\nu_5(B_1)$	1013	1010
$\nu_6(B_2)$	914	918	$\nu_6(B_2)$	915	912

Table (8). Observed binary combination frequencies and assignments for sodium formate-d.

Solution		
Observed	Assignment	Calculated
2895	$\nu_2 + \nu_4$	2910
2344	$\nu_2 + \nu_5$ or $\nu_3 + \nu_4$	2350 2346
2031	$2\nu_5$	2048
1845	$2\nu_6$	1828

Solid (pellet)		
Observed	Assignment	Calculated
3459	$\nu_1 + \nu_2$	3467
2891	$\nu_2 + \nu_4$	2916
2831	$\nu_1 + \nu_3$	2901
2654	$2\nu_2$	2668
2346	$\nu_2 + \nu_5$ or $\nu_3 + \nu_4$	2347 2350
2090	$\nu_2 + \nu_3$	2102
2015	$2\nu_5$	2026

Solid (mull)		
Observed	Assignment	Calculated
2090	$\nu_2 + \nu_3$	2096
2014	$2\nu_5$	2024

Table (9). Comparison of frequencies and assignments for combinations of sodium formate-d.

Solution			Pellet		
Assignment	This work (I.R.)	Fonteyne (Raman)	Assignment	This work (I.R.)	Harvey et al. (I.R.)
$2\nu_6$	~1845	1831	$\nu_2+\nu_3$	2090	2080
$2\nu_5$	2021	2032	$2\nu_5$	2015	2017

Product Rule Calculations

Teller (quoted in (2)) and Redlich (20) have shown that for two isotopic molecules the product of the $\frac{\omega^{(i)}}{\omega}$ ratios for all vibrations of a given irreducible representation is independent of the potential constants and depends only upon the masses of the atoms and the geometrical structure of the molecule. The general formula for any molecule is (12):

$$\frac{\omega_1^{(i)}}{\omega_1}\frac{\omega_2^{(i)}}{\omega_2}\cdots\frac{\omega_f^{(i)}}{\omega_f} = \left[\left(\frac{m_1}{m_1^{(i)}}\right)^{\alpha}\left(\frac{m_2}{m_2^{(i)}}\right)^{\beta}\cdots\left(\frac{M^{(i)}}{M}\right)^{t}\left(\frac{I_x^{(i)}}{I_x}\right)^{\delta_x}\left(\frac{I_y^{(i)}}{I_y}\right)^{\delta_y}\cdot\left(\frac{I_z^{(i)}}{I_z}\right)^{\delta_z}\right]^{1/2} \qquad (6)$$

Here all quantities referring to the isotopic molecule are marked by the superscript (i) while the quantities referring to the originally considered "ordinary" molecule do not have this superscript; ω_1, ω_2, ..., ω_f are the (zero-order) frequencies of the f genuine vibrations of the irreducible representation considered; m_1, m_2, ... are the masses of the representative

atoms of the various sets (each set consisting of atoms that are geometrically transformed into one another by the symmetry operations permitted by the molecule). The exponents α, β, ... are the number of vibrations (inclusive of non-genuine vibrations, i.e., translation and rotation) contributed by each set of equivalent atoms (i.e., the N_k^j already introduced). M is the total mass of the molecule; t is the number of translations belonging to the irreducible representation considered. I_x, I_y, I_z are the moments of inertia about the x, y, and z axes through the center of mass; δx, δy, δz are 1 or 0 depending on whether R_x, R_y, R_z belong to the irreducible representation considered. For the formate-d ion α and β have already been calculated as N_k^j. The values of t and the δ's may be deduced from the C_{2v} point group character table for irreducible representations. The results are shown in Table (10).

Table (10). α, β, t, δx, δy, δz values for formate-d ion.

	A_1	B_1	B_2
α	1	1	1
β	1	1	1
t	1	1	1
δx	0	0	1
δy	0	1	0
δz	0	0	0

Figure (13) shows the distances involved in the calculation of the moments of mertia I_x and I_y, where the x and y axes are defined as in Fig. (1). Since $\delta z = 0$ for all three irreducible representations it is not necessary to calculate I_z. I_x and I_y are defined by the following equations:

$$I_x = m_D z^2 + m_C x^2 + 2m_O w^2 \qquad (7)$$

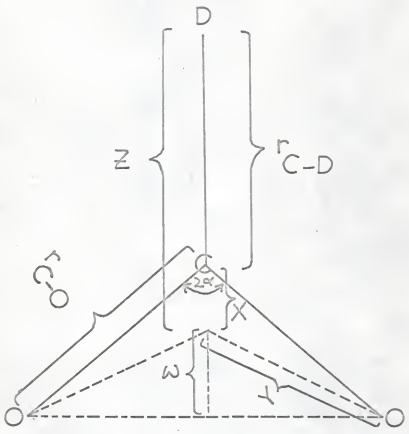


Figure 13. Diagrammatic illustration of various parameters used in Product-rule calculations.

$$I_y = m_D z^2 + m_C x^2 + 2m_O y^2 \tag{8}$$

where m_D, m_C, and m_O are the masses of the deuterium, carbon, and oxygen atoms, respectively.

As shown in Fig. (13).

$$x + w = r_{C-O} \cos(\alpha/2) \tag{9}$$

$$y = \left[w^2 + (r_{C-O} \cos(\alpha/2))^2\right]^{1/2} \tag{10}$$

$$z = r_{C-D} + x \tag{11}$$

Using the torque equation

$$z\, m_D + x\, m_C = 2w\, m_O \tag{12}$$

with (9) and (11) yields

$$x = \frac{2m_O\, r_{C-O} \cos(\alpha/2) - r_{C-D}\, m_D}{m_D + m_C + 2m_O} \tag{13}$$

The calculation of x from equation (13) was made using the molecular geometry from the X-Ray diffraction study of Zacharisen (26), who assumed a C-H distance of 0.99A° and obtained a C-O distance of 1.27A° and an OCO angle of 124°. It is assumed here that the C-D and C-H distances are equal. Since r_{C-H} = 0.99 A° seems small in view of the fact that r_{C-H} = 1.09 A° in formic acid (21), calculations were made using both r_{C-D} = 0.99 A° and 1.09 A°.

The resulting values of I_x and I_y for the formate, formate-d and formate-^{13}C are shown in Table (11). Tables (12) and (13) list the fundamentals previously measured and assigned (6) for the formate and formate-^{13}C ions, respectively.

Table (11). Moments of inertia values for the three formate ions.

	I_x (AMU-A^2)		I_y (AMU-A^2)	
	r_{C-H}*		r_{C-H}*	
	0.99 A°	1.09 A°	0.99 A°	1.09 A°
formate	5.1005	5.3909	45.334	45.625
formate-d	7.0074	7.5752	47.242	47.809
formate-^{13}C	5.2589	5.5476	45.497	45.785

*$r_{C-H} = r_{C-D} = r_{^{13}C-H}$ is assumed in calculations.

Table (12). Observed frequencies and assignments for fundamentals of sodium formate.

Assignment	Solution	Mull	Pellet
ν_1 (A_1)	2816	2830	2828
ν_2 (A_1)	1352	(1364)*	(1364)*
ν_3 (A_1)	769	774	773
ν_4 (B_1)	1593	1593	1600
ν_5 (B_1)	1384	(1364)*	(1364)*
ν_6 (B_2)		1070	1070

*Numbers in parentheses refer to frequencies that could not be resolved.

Table (13). Observed frequencies and assignments for fundamentals of sodium formate-$^{13}C°$.

Assignment	Solution	Mull	Pellet
ν_1 (A_1)	(2813)*	2818	2818
ν_2 (A_1)	1332	1336	1338
ν_3 (A_1)	(767)*	766	766
ν_4 (B_1)	1547	1559	1560
ν_5 (B_1)	(1384)*	(1363)*	(1364)*
ν_6 (B_2)		1054	1054

*Numbers in parentheses refer to frequencies that could not be resolved.

Tables (14), (15), (16) give theoretical frequency product ratios and observed frequency product ratios for various combinations of the three isotopic formate ions. Wherever a range of the theoretical frequency product ratio is given, the lower value corresponds to r_{C-H} of 0.99 A° and the upper value to r_{C-H} of 1.09 A°. The observed frequency product ratios were calculated from the frequency data presented in Tables (6), (12) and (13).

Table (14). Theoretical frequency product ratios and some observed frequency ratios for sodium formate-d and sodium formate.

Irreducible representation	Frequency product ratios			
	Observed			Theoretical
	Solution	Mull	Pellet	
A_1	0.730	0.726	0.733	$\nu_1 \times \nu_2 \times \nu_3$ 0.715
B_1	0.736	0.735	0.734	$\nu_4 \times \nu_5$ 0.730
B_2	0.855	0.853	0.855	ν_6 0.732 0.838 0.848

Table (15). Theoretical frequency product ratios and some observed frequency ratios for sodium formate-d and C-13 enriched sodium formate.

Irreducible representation	Frequency product ratios			
	Observed			Theoretical
	Solution	Mull	Pellet	
A_1	0.744	0.752	0.757	$\nu_1 \times \nu_2 \times \nu_3$ 0.737
B_1	0.758	0.752	0.753	$\nu_4 \times \nu_5$ 0.750
B_2		0.866	0.868	ν_6 0.850 0.860

Table (16). Theoretical and experimental product ratios and some observed frequency ratios for sodium formate and C-13 enriched sodium formate.

Irreducible representation	Frequency product ratios			
	Observed			Theoretical
	Solution	Mull	Pellet	
A_1		0.985	0.987	0.971
B_1	0.971	0.979	0.975	0.973
B_2		0.985	0.985	0.986

It may be noted that the product rule is based on the assumption of identical force fields for isotopic molecules, which is practically always fulfilled. On this assumption the product rule should hold rigorously for the zero-order frequencies ω_i and at least to a good approximation for the observed fundamentals ν_i for any mass difference. One can also predict the direction of deviation in case the ν_i rather than the ω_i are used. If (i) refers to the heavier isotope, then since for it the anharmonicity constants $x_{ik}^{(i)}$ are smaller than x_{ik}, and therefore $\omega_i^{(i)} - \nu_i^{(i)}$ is smaller than $\omega_i - \nu_i$, the product $\frac{\nu_1^{(i)}}{\nu_1} \frac{\nu_2^{(i)}}{\nu_2} \cdots \frac{\nu_f^{(i)}}{\nu_f}$ should be slightly greater than the right-hand side of equation (6).

All previous investigators (5, 18, 15, 6) agree on the assignment for ν_1, ν_3, ν_4, and ν_6. The disagreement is in the assignments of ν_2 and ν_5 with three of the four assignments (5, 15, 6) placing ν_5 above ν_2. The observed frequency product ratios in Tables (14) and (15) support the assignment of ν_5 to a higher frequency than ν_2. In every case the observed ratios are slightly larger than the theoretical ratios, as expected, since observed fundamentals rather than zero order frequencies have been used. The reversal of the ν_2 and ν_5 assignments given in Table 6 for the formate-d ion will make the observed frequency product ratio much too low for the A_1 irreducible representation and much too high for the B_1 irreducible representation. Thus, the assignment for the formate-d ion may be made with confidence. The situation is not this clear cut for the other isotopic formate ions due to failure to resolve several fundamentals for the formate-^{13}C ion in solution and for the formate ion in mulls and pellets. The most reliable comparisons are between the formate and formate-d for solution and between the formate-d

and formate-^{13}C ions for assignments in mulls and pellets. Table (17) compares observed product ratios from Tables (14) and (15) with observed product ratios using the reverse assignments of $\nu_2 > \nu_5$. For solution assignment 2 may be rejected because the observed frequency product ratio is less than the theoretical ratio for the A_1 irreducible representation, while all observed ratios are expected to be greater than the theoretical ratio. For mulls and pellets both assignments give observed ratios somewhat greater than the theoretical ratios, as expected. Here assignment 1 is also favored because the A_1 irreducible representation with three fundamentals is expected to have a larger deviation from theory than the B_1 irreducible representation with only two fundamentals. Assignment 1 conforms to this expectation while assignment 2 does not.

Force Constant Calculations

For an XYZ_2 molecule, the potential energy, under the assumption of valence forces, is:

$$2V = k_1 q_{14}^2 + k_2 (q_{12}^2 + q_{13}^2) + k_\delta \delta_{23}^2 + k_\delta' (\delta_{24}^2 + \delta_{34}^2) + k_\Delta \Delta^2 \quad (14)$$

where the nuclei are numbered as indicated in Fig. (14). The q_{ij} and δ_{ij} are changes in distance and angle, respectively, between atoms i and j. The force constants k_1 and k_2 represent the resistance to stretching of the X-Y and Y-Z bonds, respectively, k_δ refers to the change in angle between the two Y-Z bonds, k_δ' to the change in angle between the X-Y and Y-Z bonds, and k_Δ to the change Δ of the angle between the X-Y bond and the YZ_2 plane. Herzberg (13) has reported the following equations relating the observed fundamental frequencies to the valence force field potential constants.

Table (17). Comparison of observed frequency product ratios for two possible assignments of ν_2 and ν_5.

Irreducible representation	Frequency product ratios Observed			Theoretical
		Formate-d and Formate Solution		
		assignment 1. $\nu_5 > \nu_2$		
A_1	0.730		$\nu_1 \times \nu_2 \times \nu_3$	0.715
B_1	0.736		$\nu_4 \times \nu_5$	0.730-0.732
		assignment 2. $\nu_2 > \nu_5$		
A_1	0.713		$\nu_1 \times \nu_2 \times \nu_3$	0.715
B_1	0.753		$\nu_4 \times \nu_5$	0.730-0.732
		Formate-d and Formate-^{13}C		
	Mull	Pellet		
		assignment 1. $\nu_5 > \nu_2$		
A_1	0.752	0.757	$\nu_1 \times \nu_2 \times \nu_3$	0.737
B_1	0.752	0.753	$\nu_4 \times \nu_5$	0.750
		assignment 2. $\nu_2 > \nu_5$		
A_1	0.737	0.742	$\nu_1 \times \nu_2 \times \nu_3$	0.737
B_1	0.767	0.768	$\nu_4 \times \nu_5$	0.750

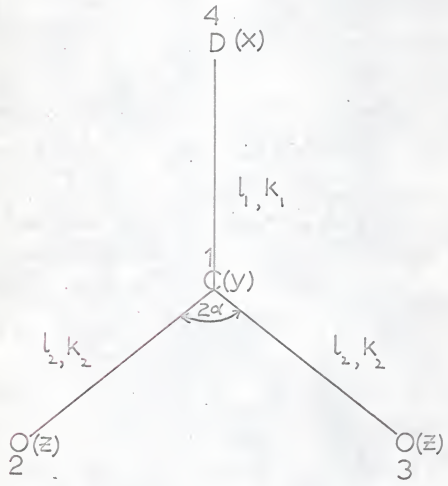


Figure 14. Diagrammatic illustration of the nuclei and some of the parameters used in force constant calculations.

$$\lambda_1+\lambda_2+\lambda_3 = k_1\left(\frac{1}{m_x}+\frac{1}{m_y}\right)+k_2\left(\frac{1}{m_z}+\frac{2}{m_y}\cos^2\alpha\right)+\frac{2k_\delta+k'_\delta}{l_2^2}\left(\frac{1}{m_z}+\frac{2}{m_y}\sin^2\alpha\right) \quad (15)$$

$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_1\lambda_3 = k_1k_2\left(\frac{1}{m_xm_z}+\frac{1}{m_ym_z}+\frac{2}{m_xm_y}\cos^2\alpha\right)$$
$$+k_1\frac{2k_\delta+k'_\delta}{l_2^2}\left(\frac{1}{m_xm_z}+\frac{1}{m_ym_z}+\frac{2}{m_xm_y}\sin^2\alpha\right)$$
$$+k_2\frac{2k_\delta+k'_\delta}{l_2^2}\left(\frac{1}{m_z^2}+\frac{2}{m_ym_z}\right) \quad (16)$$

$$\lambda_1\lambda_2\lambda_3 = k_1k_2\frac{2k_\delta+k'_\delta}{l_2^2}\left(\frac{1}{m_xm_z^2}+\frac{1}{m_ym_z^2}+\frac{2}{m_xm_ym_z}\right) \quad (17)$$

$$\lambda_4+\lambda_5 = k_2\left(\frac{1}{m_z}+\frac{2}{m_y}\sin^2\alpha\right)+\frac{k'_\delta}{l_1^2l_2^2}\left(\frac{2l_2^2}{m_x}+\frac{l_1^2}{m_z}+\frac{2(l_2+l_1\cos\alpha)^2}{m_y}\right) \quad (18)$$

$$\lambda_4\lambda_5 = k_2\frac{k'_\delta}{l_1^2l_2^2}\left(\frac{2l_2^2}{m_xm_z}+\frac{l_1^2}{m_z^2}+\frac{2(l_1^2+l_2^2)}{m_ym_z}+\frac{4l_1l_2\cos\alpha}{m_ym_z}+\frac{4l_2^2}{m_xm_y}\sin^2\alpha\right) \quad (19)$$

$$\lambda_6 = \frac{k_4}{l_1^2l_2^2\cos^2\alpha}\left(\frac{l_1^2}{2m_z}+\frac{l_2^2\cos^2\alpha}{m_x}+\frac{(l_1+l_2\cos\alpha)^2}{m_y}\right) \quad (20)$$

Here $\lambda_i = 4\pi^2c^2\nu_i^2$ where c is the velocity of light and ν_i is the frequency of the observed fundamental in $cm.^{-1}$. Equation (19) has been corrected for a misprint discovered in Herzberg when equation (19) was derived (7) using the Wilson FG matrix method (25) and shown (7) to be consistent with the Teller-Redlich product rule.

By suitable definition of D_i (i = 1 to 10), equations (15), (16), (17), (18) and (19) are reduced to equations (21), (22), (23), (24) and (25), respectively.

$$\lambda_1+\lambda_2+\lambda_3 = k_1D_6 + k_2D_7+(2k_\delta+k'_\delta)\,D_8 \tag{21}$$

$$\lambda_1\lambda_2+\lambda_2\lambda_3+\lambda_1\lambda_3 = k_1k_2D_3+(2k_\delta+k'_\delta)(k_1D_4+k_2D_5) \tag{22}$$

$$\lambda_1\lambda_2\lambda_3 = k_1k_2(2k_\delta + k'_\delta)D_9 \tag{23}$$

$$\lambda_4+\lambda_5 = k_2D_1+k'_\delta\,D_2 \tag{24}$$

$$\lambda_4\lambda_5 = k_2k'_\delta\,D_{10} \tag{25}$$

The D_i's are defined as follows (i = 1, ..., 10)

$$D_1 = \frac{1}{m_z} + \frac{2}{m_y}\sin^2\alpha \tag{26}$$

$$D_2 = \frac{1}{l_1^2l_2^2}\left(\frac{2l_2^2}{m_x} + \frac{l_1^2}{m_z} + \frac{2(l_2+l_1\cos\alpha)^2}{m_y}\right) \tag{27}$$

$$D_3 = \frac{1}{m_xm_z} + \frac{1}{m_ym_z} + \frac{2}{m_xm_y}\cos^2\alpha \tag{28}$$

$$D_4 = \frac{1}{l_2^2}\left(\frac{1}{m_xm_z} + \frac{1}{m_ym_z} + \frac{2}{m_xm_y}\sin^2\alpha\right) \tag{29}$$

$$D_5 = \frac{1}{l_2^2}\left(\frac{1}{m_z^2} + \frac{2}{m_ym_z}\right) \tag{30}$$

$$D_6 = \frac{1}{m_x} + \frac{1}{m_y} \tag{31}$$

$$D_7 = \frac{1}{m_z} + \frac{2}{m_y}\cos^2\alpha \tag{32}$$

$$D_8 = \frac{1}{l_2^2}\left(\frac{1}{m_z} + \frac{2}{m_y}\sin^2\alpha\right) \tag{33}$$

$$D_9 = \frac{1}{l_2^2}\left(\frac{1}{m_xm_z^2} + \frac{1}{m_ym_z^2} + \frac{2}{m_xm_ym_z}\right) \tag{34}$$

$$D_{10} = \frac{1}{l_1^2l_2^2}\left(\frac{2l_2^2}{m_xm_z} + \frac{l_1^2}{m_z^2} + \frac{2(l_1^2+l_2^2)}{m_ym_z} + \frac{4l_1l_2\cos\alpha}{m_ym_z} + \frac{4l_2^2\sin^2\alpha}{m_xm_y}\right) \tag{35}$$

A Fortran program has been written to calculate most of the D_i's required for the three isotopic formate ions. The program appears in Appendix I. The calculations were carried out using the IBM 1620 system. In addition this program has been used to calculate k_Δ from equation (20).

Table (18) gives values of D_i's for the three isotopic formate ions for $r_{C-H} = 0.99$ A°.

Table (19) gives values of D_i's for the three isotopic formate ions for $r_{C-H} = 1.09$ A°.

A Fortran program has been written to calculate k_2 and k'_δ (called CK2 and CKP in the program output) from equations (24) and (25) and k_1 and k_δ (called CK1 and CKD in the program output) from equations (21) and (22) using the D_i values reported in Tables (18) and (19). There are two places in the program (CK2 and CK1) where either a + or - sign is permissible. On the basis of physically reasonable force constant values, the calculations show that both signs should be chosen as positive. Calculations were carried out on the IBM 1410 computer. Results for the five force constants are shown in Tables (20), (21) and (22).

An additional Fortran program has been written to calculate k_1 and k_δ (called CK1 and CKP in the program output) from equations (21) and (23). The first part of this additional program is identical with previous programs in calculating k_2 and k'_δ (called CK_2 and CKP in the program output) from equations (24) and (25). As before D_i values reported in Tables (18) and (19) were used and the calculations were carried out using the IBM 1410 computer. Results for the five force constants are shown in Tables (23), (24) and (25).

The agreement between k_1 and k_δ values calculated by equations (21) and (22) and equations (21) and (23) is satisfactory; all of the force constant values reported in Tables (20), (21), (22), (23), (24), and (25)

Table (18). D_i's for formate-d, formate and C-13 formate ions.*

	$D_1 \times 10^{-23}$	$D_2 \times 10^{-40}$	$D_3 \times 10^{-46}$	$D_4 \times 10^{-62}$	$D_5 \times 10^{-61}$	$D_6 \times 10^{-23}$	$D_7 \times 10^{-22}$	$D_8 \times 10^{-38}$	$D_9 \times 10^{-85}$	$D_{10} \times 10^{-40}$
formate-d	1.16	0.82	1.98	2.27	3.22	3.49	5.98	7.19	1.01	0.72
formate	1.16	1.43	3.76	4.41	3.22	6.48	5.98	7.19	1.97	1.03
C-13 formate	1.10	1.42	3.65	4.18	3.04	6.44	5.81	6.81	1.85	1.00

*r_{C-H} = 0.99 A°.

Table (19). D_i's for formate-d, formate and C-13 formate ions.*

	$D_1 \times 10^{-23}$	$D_2 \times 10^{-40}$	$D_3 \times 10^{-46}$	$D_4 \times 10^{-62}$	$D_5 \times 10^{-61}$	$D_6 \times 10^{-23}$	$D_7 \times 10^{-22}$	$D_8 \times 10^{-38}$	$D_9 \times 10^{-85}$
formate-d	1.16	0.69	1.98	2.27	3.22	3.49	5.98	7.19	1.01
formate	1.16	1.20	3.76	4.41	3.22	6.48	5.98	7.19	1.97
C-13 formate	1.10	1.18	3.65	4.18	3.04	6.44	5.81	6.81	1.85

*r_{C-H} = 1.09 A°.

Table (20). Formate-d ion: force constants* calculated from equations (20), (21), (22), (24) and (25).

	$k_1 x10^{-5}$	$k_2 x10^{-5}$	$k_\delta x10^{11}$	$k'_\delta x10^{12}$	$k_\Delta x10^{12}$
Solution (0.99 A°)	4.19	6.10	3.77	6.74	4.11
Solution (1.09 A°)	4.18	5.93	3.79	8.30	4.61
Pellet (0.99 A°)	4.26	6.20	3.82	6.46	4.12
Pellet (1.09 A°)	4.25	6.08	3.82	7.91	4.62
Mull (0.99 A°)	4.27	6.17	3.80	6.46	4.10
Mull (1.09 A°)	4.27	6.04	3.79	7.91	4.60

*k_1, k_2 are expressed as dynes/cm., while k_δ, k'_δ, k_Δ have the units dynes. cm./radian.

Table (21). C-13 formate ion: force constants* calculated from equations (20), (21), (22), (24) and (25).

	$k_1 x10^{-5}$	$k_2 x10^{-5}$	$k_\delta x10^{11}$	$k'_\delta x10^{12}$	$k_\Delta x10^{12}$
Solution (0.99 A°)	4.30	8.87	2.42	4.54	3.95
Solution (1.09 A°)	4.30	8.92	2.35	5.44	4.54
Pellet (0.99 A°)	4.32	8.76	2.50	4.54	3.95
Pellet (1.09 A°)	4.32	8.82	2.43	5.44	4.54
Mull (0.99 A°)	4.32	8.75	2.49	4.54	3.95
Mull (1.09 A°)	4.32	8.80	2.42	5.43	4.54

*k_1, k_2 are expressed as dynes/cm., while k_δ, k'_δ, k_Δ have the unit dynes. cm./radian.

Table (22). Formate ion: force constants* calculated from equations (20), (21), (22), (24) and (25).

	$k_1 x10^{-5}$	$k_2 x10^{-5}$	$k_\delta x10^{11}$	$k'_\delta x10^{12}$	$k_\Delta x10^{12}$
Solution (0.99 A°)	4.28	8.71	2.42	4.64	3.96
Solution (1.09 A°)	4.28	8.77	2.35	5.56	4.54

*k_1, k_2 are expressed as dynes/cm., while k_δ, k'_δ, k_Δ have the unit dynes. cm./radian.

Table (23). Formate-d ion: force constants* calculated from equations (20), (21), (23), (24) and (25).

	$k_1 x10^{-5}$	$k_2 x10^{-5}$	$k_\delta x10^{11}$	$k'_\delta x10^{12}$	$k_\Delta x10^{12}$
Solution (0.99 A°)	4.29	6.10	3.54	6.74	4.11
Solution (1.09 A°)	4.26	5.93	3.60	8.30	4.61
Pellet (0.99 A°)	4.36	6.20	3.59	6.46	4.12
Pellet (1.09 A°)	4.34	6.08	3.62	7.91	4.62
Mull (0.99 A°)	4.37	6.17	3.56	6.46	4.10
Mull (1.09 A°)	4.35	6.04	3.59	7.91	4.60

*k_1, k_2 are expressed as dynes/cm., while k_δ, k'_δ, k_Δ have the unit dynes. cm./radian.

Table (24). C-13 Formate ion: force constants* calculated from equations (20), (21), (23), (24) and (25).

	$k_1 \times 10^{-5}$	$k_2 \times 10^{-5}$	$k_\delta \times 10^{11}$	$k'_\delta \times 10^{12}$	$k_\Delta \times 10^{12}$
Solution (0.99 A°)	4.31	8.87	2.37	4.54	3.95
Solution (1.09 A°)	4.31	8.92	2.31	5.44	4.54
Pellet (0.99 A°)	4.34	8.76	2.41	4.54	3.95
Pellet (1.09 A°)	4.34	8.82	2.35	5.44	4.54
Mull (0.99 A°)	4.34	8.75	2.41	4.54	3.95
Mull (1.09 A°)	4.33	8.80	2.35	5.43	4.54

*k_1, k_2 are expressed as dynes/cm., while k_δ, k'_δ, k_Δ have the unit dynes. cm./radian.

Table (25). Formate ion: force constants* calculated from equations (20), (21), (23), (24) and (25).

	$k_1 \times 10^{-5}$	$k_2 \times 10^{-5}$	$k_\delta \times 10^{11}$	$k'_\delta \times 10^{12}$	$k_\Delta \times 10^{12}$
Solution (0.99 A°)	4.29	8.71	2.37	4.64	3.96
Solution (1.09 A°)	4.29	8.77	2.31	5.56	4.54

*k_1, k_2 are expressed as dynes/cm., while k_δ, k'_δ, k_Δ have the units dynes. cm./radian.

are physically reasonable. There appear to be no reports in the literature of force constant calculations for the formate ion using a correct assignment of fundamentals with a valence force field. Fonteyne (5) has reported a calculation using nine potential constants with Raman data for the formate and formate-d ions in aqueous solution. The five major force constants in Fonteyne's calculation are compared in Table (26) with the average aqueous solution results for r_{C-H} = 1.09 A° from Tables (20), (22), (23) and (25). The order of magnitude agreement between Fonteyne's results and those of this work is satisfactory in view of the different forms of the potential energy assumed. The large absolute magnitude of the difference in k_2 obtained for the formate and formate-d ions is almost certainly caused by a deficiency in the valence force field description of the vibrational potential energy of the formate ion.

Table (26). Comparison of force constants for aqueous solution samples.

Force constants	Fonteyne (5)	This work	
		formate ion	formate-d ion
$k_1 \times 10^{-5}$ dynes./cm.	4.66	4.28	4.22
$k_2 \times 10^{-5}$ dynes./cm.	8.12	8.77	5.93
$k_\delta \times 10^{11}$ $\frac{\text{dynes./cm.}}{\text{radian}}$	6.51	2.33	3.60
$k'_\delta \times 10^{11}$ $\frac{\text{dynes./cm.}}{\text{radian}}$	1.36	0.556	0.830

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LITERATURE CITED

1. A. Adel and E. F. Barker, Phys. Rev., 44, 99 (1933).

2. W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, J. Chem. Soc. 1936, 971.

3. N. Bjerrum, Verh. d.d. Phys. Ges., 16, 737 (1914).

4. H. Bethe, Ann. Physik, 3, 133, (1929).

5. R. Fonteyne, Natuurw. Tijdschr. (Ghent), 25, 173 (1943).

6. R. M. Hammaker and J. P. Walters, Spectrochim. Acta, 20, 1311 (1964).

7. R. M. Hammaker, Private Communication.

8. K. B. Harvey, B. A. Morrow, and H. F. Shurvell, Can. J. Chem., 41, 1181 (1963).

9. G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules." D. Van Nostrand Company, Inc. Princeton, New Jersey, 1945, p. 239.

10. Ibid., p. 159.

11. Ibid., pp. 65-67.

12. Ibid., p. 232.

13. Ibid., p. 180.

14. J. O. Hirschfelder, J. Chem. Phys., 6, 795 (1933).

15. K. Ito and H. J. Bernstein., Can. J. Chem., 34, 179 (1956).

16. J. Lecomte, Compte. Rend., 208, 1401 (1939).

17. J. Lecomte, Cahiers Phys., 17, 1 (1943).

18. R. Newman, J. Chem. Phys., 20, 1663 (1952).

19. K. S. Pitzer, "Quantum Chemistry," Prentice Hall, Inc., Englewood Cliffs, N. J., 1953, p. 450.

20. O. Redlich, Z. Physik. Chem., B. 28, 371 (1935).

21. L. E. Sutton, "Interatomic Distances," Special Publication No. 11. The Chemical Society, Burlington House, London, 1956, p. 109.

22. O. Thomas, Disc. Faraday Soc., 9, 339 (1950).

23. E. Wigner, Nachr. Ges. Wiss. Göttingen, p. 133 (1930).

24. E. B. Wilson Jr., J. C. Decius, and Paul C. Cross, "Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra," McGraw Hill Book Company, Inc. New York, Toronto, London, 1955, p. 1.

25. Ibid.

26. W. H. Zacharisen, J. Am. Chem. Soc., 62, 1011 (1940).

APPENDIX I

Fortran program (run on IBM 1620 computer) to calculate D_i's and k_Δ

```
    READ 21, A1
 21 FORMAT (14.8)
    READ 15,X,Y
 15 FORMAT (2E14.8)
121 READ 11,V1,V2,V3,V4,V5,V6
 11 FORMAT (6F6.0)
    C=.29979300E+11
    Z=.16000000E+02/.60248000E+24
    A2=.12700000E-07
    S1=.46947000E+00
    S2=.88295000E+00
    B1=4.*(3.14159)**2*C**2*(V1)**2
    B2=4.*(3.14159)**2*C**2*(V2)**2
    B3=4.*(3.14159)**2*C**2*(V3)**2
    B4=4.*(3.14159)**2*C**2*(V4)**2
    B5=4.*(3.14159)**2*C**2*(V5)**2
    B6=4.*(3.14159)**2*C**2*(V6)**2
    PUNCH 5,B1,B2,B3
    PUNCH 5,B4,B5,B6
  5 FORMAT(3E14.8)
    BOB=B6*A1**2*A2**2*S1**2
    DAY=(A1**2)/(2.*Z)+((A2**2)*S1**2)/X+((A1+A2*S1)**2)/Y
    CK5=BOB/DAY
    PUNCH 7,CK5
  7 FORMAT(E14.8)
    SU=B4*B5*A1**2*A2**2
    WU=(2.*A2**2)/(X*Z)+(A1**2)/(Z**2)+(2.*(A1**2+A2**2))/(Y*Z)
    HOU=(4.*A1*A2*S1)/(Y*Z)+(4.*A2**2*S2**2)/(X*Y)
    CK4=SU/(WU+HOU)
    PUNCH 7,CK4
    D1=1./Z+(2.*S2**2)/Y
    PUNCH 7,D1
    DAWN=(2.*A2**2)/X+(A1**2)/Z+(2.*(A2+A1*S1)**2)/Y
    SUN=A1**2*A2**2
    D2=DAWN/SUN
    PUNCH 7,D2
    D3=1./(X*Z)+1./(Y*Z)+(2.*S1**2)/(X*Y)
    D4=(1./(X*Z)+1./(Y*Z)+(2.*S2**2)/(X*Y))/(A2**2)
    D5=(1./(Z**2)+2./(Y*Z))/(A2**2)
    PUNCH 9,D3,D4,D5
  9 FORMAT(3E14.8)
    D6=(1./X)+1./Y
    D7=1./Z+(2.*S1**2)/Y
    D8=(1./Z+(2.*S2**2)/Y)/(A2**2)
    PUNCH 9,D6,D7,D8
    GO TO 121
    END
```

APPENDIX II

Fortran program (run on IBM 1410 computer) to evaluate force constants using equations (21), (22), (24) and (25).

```
    DIMENSIONTITLE(12)
  1 FORMAT(12 A6)
  2 FORMAT(1HL,12A6)
  3 FORMAT(3E14.8)
  4 FORMAT(1H ,1P4(E15.8,2X))
  5 FORMAT(7HKLAMBDA)
  6 FORMAT(5HKD(I))
  7 FORMAT(4HLK1=,1PE15.8,7H    K2=,E15.8)
  8 FORMAT(8HKKDELTA=,1PE15.8,12H    KDPRIME=,E15.8)
  9 FORMAT(7HKKCAPD=,1PE15.8)
 11 READ(1,1)(TITLE(I),I=1,12)
    WRITE(3,2)(TITLE(I),I=1,12)
    READ(1,3)Y1,Y2,Y3
    IF(Y1.EQ.0.)STOP
    READ(1,3)Y4,Y5,Y6
    READ(1,3)CKCD
    READ(1,3)CK4
    READ(1,3)D1
    READ(1,3)D2
    READ(1,3)D3,D4,D5
    READ(1,3)D6,D7,D8
    WRITE(3,5)
    WRITE(3,4)Y1,Y2,Y3,Y4
    WRITE(3,4)Y5,Y6
    WRITE(3,6)
    WRITE(3,4)D1,D2,D3,D4
    WRITE(3,4)D5,D6,D7,D8
    AY=Y4+Y5
    CK2=(AY+SQRT(AY*AY-4.*D1*D2*CK4))/(2.*D1)
    CKP=CK4/CK2
    CY=Y1*Y2+Y2*Y3+Y1*Y3
    BY=Y1+Y2+Y3
    BQ=(CK2*(D5*D6+D4*D7-D3*D8)*1.E-98)-(BY*D4*1.E-98)
    A=D4*D6*1.E-98
    C=(-BY*CK2*D5+CK2*CK2*D5*D7+D8*CY)*1.E-98
    CK1=(-BQ+SQRT(BQ*BQ-4.*A*C))/(2.*A)
    BR=(CY*1.E-98)-(CK1*CK2*D3*1.E-98)-(CK1*CKP*D4*1.E-98)-(CK2*CKP*D5
   1*1.E-98)
    BS=2.*(CK1*D4+CK2*D5)*1.E-98
    CKD=BR/BS
    WRITE(3,7)CK1,CK2
    WRITE(3,8)CKD,CKP
    WRITE(3,9)CKCD
    GO TO 11
    END
```

APPENDIX III

Fortran program (run on IBM 1410 computer) to evaluate force constants using equations (21), (23), (24) and (25)

```
    DIMENSIONTITLE(12)
  1 FORMAT(12 A6)
  2 FORMAT(1HL,12A6)
  3 FORMAT(3E14.8)
  4 FORMAT(1H ,1P4(E15.8,2X))
  5 FORMAT(7HKLAMBDA)
  6 FORMAT(5HKD(I))
  7 FORMAT(4HLK1=,1PE15.8,7H    K2=,E15.8)
  8 FORMAT(8HKKDELTA=,1PE15.8,12H    KDPRIME=,E15.8)
  9 FORMAT(7HKKCAPD=,1PE15.8)
 11 READ(1,1)(TITLE(I),I=1,12)
    WRITE(3,2)(TITLE(I),I=1,12)
    READ(1,3)Y1,Y2,Y3
    IF(Y1.EQ.0.)STOP
    READ(1,3)Y4,Y5,Y6
    READ(1,3)CKCD
    READ(1,3)CK4
    READ(1,3)D1
    READ(1,3)D2
    READ(1,3)D3,D4,D5
    READ(1,3)D6,D7,D8
    READ(1,3)D9
    WRITE(3,5)
    WRITE(3,4)Y1,Y2,Y3,Y4
    WRITE(3,4)Y5,Y6
    WRITE(3,6)
    WRITE(3,4)D1,D2,D3,D4
    WRITE(3,4)D5,D6,D7,D8
    WRITE(3,4)D9
    AY=Y4+Y5
    CK2=(AY+SQRT(AY*AY-4.*D1*D2*CK4))/(2.*D1)
    CKP=CK4/CK2
    DY=Y1*Y2*Y3
    BY=Y1+Y2+Y3
    BT=(CK2*CK2)*(D9*1.E-98)*D7-(BY*CK2)*(D9*1.E-98)
    A=(D6*CK2)*(D9*1.E-98)
    C=D8*(DY*1.E-98)
    CK1=(-BT+SQRT(BT*BT-4.*A*C))/(2.*A)
    CKD=((DY*1.E-98)-(CK1*CK2*CKP)*(D9*1.E-98))/(2.*(CK1*CK2)*(D9*1.E-
   198))
    WRITE(3,7)CK1,CK2
    WRITE(3,8)CKD,CKP
    WRITE(3,9)CKCD
    GO TO 11
    END
```

APPENDIX IV

Check on PE 221 linearity. Frequency of polystyrene peak at 1946 relative to CO lines assuming linear scale.

CO Frequency	Polystyrene Frequency
2139.4	1940.9
2135.6	1940.8
2131.6	1940.6
2123.7	1940.6
2119.7	1940.7
2111.6	1940.9
2094.9	1941.1
2090.6	1940.9
2086.3	1940.8
2082.0	1940.7
2077.7	1940.8
2068.9	1940.5
2059.9	1940.5
2041.7	1941.3
2037.0	1941.6
2032.3	1941.9

INFRARED SPECTRA OF SODIUM FORMATE-d

by

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The infrared spectra of sodium formate-d in solution, in mull and in pellet have been obtained. This study was carried out to complete the infrared investigation of the three isotopic ions formate, formate-^{13}C and formate-d and to permit three separate product rule calculations (formate with formate-d, formate with formate-^{13}C, and formate-^{13}C with formate-d) as a check on the assignment of fundamentals. The assignment for the formate-d ion is definitely established. Previous assignments for the formate and formate-^{13}C ions are supported. Force constant calculations based on the valence force field have been carried out. The resulting constants are physically reasonable; however, a significant deviation between force constants calculated for the formate and formate-d ions shows the valence force field to be inadequate.